Letters to the Editor

The Ordering Reaction in Co-Pt Alloys†

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An ordering reaction can occur in binary alloys of cobalt and platinum whose composition is near 50 atomic percent. The maximum temperature of order is about 825°C for the 50 atomic percent alloy and lower for those off this composition. No other reaction occurs below the maximum temperature of order. The unit cell is face-centered cubic above this temperature and ordered face-centered tetragonal below. In some respects this reaction has for its prototype the one found in the CuAu alloy.

Evidence is given which indicates that at certain temperatures and compositions the ordering reaction proceeds through a two-phase stage that by holding within a measurable temperature range discreet regions of order and of disorder may be caused to exist together in equilibrium.

On the basis of preliminary evidence, it appears that at an early stage of the ordering process, coherency between regions of order and of disorder may exist. Lattice straining, induced as a consequence of this, may account for the unusual physical properties which develop during the course of the ordering process. Thus, the process may resemble that of solid solution percipitation (aging) in its effect on certain physical properties.

Further study of the alloy is in progress.

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Impedance Synthesis without Use of Transformers

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Let $Z(s)$ be termed a B(rune) function if: (1) it is a rational function; (2) it is real for real s; and (3) the real part of Z is positive when the real part of s is positive. In his significant thesis, O. Brune[1] shows that the driving-point impedance of a passive network is a B function of the complex frequency variable s. Conversely, he shows that any B function can be realized by some passive network and gives rules for constructing such a network. In this synthesis he is forced to employ transformers with perfect coupling. It is recognized by Brune and others that the introduction of perfect transformers is objectionable from an engineering point of view. Prior to Brune, R. M. Foster[2] had shown how to synthesize the driving-point impedance of networks containing no resistors by simple series-parallel combinations of inductors and capacitors. This note gives a similar synthesis of an arbitrary impedance by series-parallel combinations of inductors, resistors, and capacitors.

A B function can be expressed as the ratio of two polynomials without common factor. Let the "rank" be the sum of the degrees of these polynomials. Obviously any B function of rank 0 can be synthesized. Suppose, then, it has been shown that all B functions of rank lower than n can be synthesized, and let $Z(s)$ be a B function of rank n. Brune gives four rules for carrying out a mathematical induction to a B function of lower rank:

(a) If Z has a pole on the imaginary axis, then Z can be synthesized by a parallel resonant element in series with an impedance Z' of lower rank; $Z=1/(cs+1/ls)+Z'$ where l^{-1}, $c\geq 0$.

(b) If Z has a zero on the imaginary axis, then Z can be synthesized by a series resonant element in parallel with an impedance Z' of lower rank; $1/Z=1/(ls+1/cs)+1/Z'$ where l, $c^{-1}\geq 0$.

(c) If the real part of Z does not vanish on the imaginary axis, $Z=r+Z_0$ where r is a positive constant (to be interpreted as resistance) and Z_0 is a B function of no greater rank than Z.

Brune's fourth rule, (d), which employs the perfect transformer, we replace by the following procedure:

(d′) If none of these reductions are possible, there exists a $w>0$ such that $Z(iw)$ is purely imaginary. First assume that $Z(iw)=iwL$ with $L>0$. We now make use of a key theorem discovered by P. I. Richards.[3] Let k be a positive number, and let

$$R(s)=\frac{kZ(s)-sZ(k)}{kZ(k)-sZ(s)}. \tag{1}$$

Then $R(s)$ is a B function whose rank does not exceed the rank of $Z(s)$. Richards states this theorem for $k=1$; the above form is an obvious modification, because $Z(ks)$ is also a B function. Let k satisfy the equation $L=Z(k)/k$. This is clearly always possible, because the function on the right varies from ∞ to 0 as k varies from 0 to ∞. With this choice of k, clearly $R(iw)=0$. Solving (1) for Z gives

$$\begin{aligned} Z(s)&=(1/Z(k)R(s)+s/kZ(k))^{-1}+(k/Z(k)s+R(s)/Z(k))^{-1} \\ &=(1/Z_1(s)+Cs)^{-1}+(1/Ls+1/Z_2)^{-1}. \end{aligned} \tag{2}$$

Here $Z_1(s)=kLR(s)$, $Z_2(s)=kL/R(s)$, $C=1/k^2L$. Since Z_1 is a B function with a zero on the imaginary axis, it can be synthesized. Likewise, Z_2 is a B function with a pole on the imaginary axis and can be synthesized. $Z(s)$ is therefore synthesized by two networks in series. The first network consists of the impedance Z_1 in parallel with a capacitor C, and the second network consists of the impedance Z_2 in parallel with an inductor L. In the case that $Z(iw)=-iwL$, similar considerations applied to the function $1/Z$ show that Z is synthesized by two networks in parallel. The synthesized network finally resulting has the configuration of a tree whose branches are ladder networks.

Richards[4] has sought necessary and sufficient conditions for the driving-point impedance of resistor-transmission-line circuits by means of an ingenious transformation of the Brune theory. The perfect transformers, which are again found to be objectionable, may be dispensed with by the above procedure.

[1] O. Brune, J. Math. and Phys. 10, 191–236 (1931).
[2] R. M. Foster, Bell Syst. Tech. J. 3, 259 (1924).
[3] P. I. Richards, Duke Math. J. 14, 777–786 (1947).
[4] P. I. Richards, Proc. I.R.E. 36, 217–220 (1948).

An Improvement in the Shadow-Cast Replica Technique

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Williams and Backus[1] have recently discussed in full detail the shadow-cast replica technique of electron microscopy. In the course of an investigation of the reactions of proteins in thin films,[2,3] we have performed some experiments with this technique embodying an improvement which we wish to report.

In this technique, a thin film of a metal such as chromium or uranium is deposited at an oblique angle onto the surface to be examined, by evaporation in a high vacuum. One method of removing this replica from the surface involves first, the deposition of a thin film (about 1000A) of parlodion on top of the metal film,

and second, the stripping of the parlodion and metal films together, with the aid of scotch tape.

Fine screens are placed on the scotch tape prior to stripping, so that afterwards, the screen with the replica film is disengaged and inserted in the microscope for observation.

The success of this stripping procedure depends on, among other things, the relative adhesions of the parlodion to the metal film, and the metal film to the underlying surface. We have found that ethyl cellulose*** films cast from a one percent solution in ethylene chloride are much more effective than parlodion films for this purpose, and moreover behave well in the electron microscope. In a number of instances, ethyl cellulose-backed chromium replicas were easily stripped from surfaces that completely retained those backed with parlodion. For example, three or five monolayers of barium stearate on a thin aluminum film on glass; one to six monolayers of bovine serum albumin on such a barium stearate surface; and a considerable number of similar surfaces, all behaved in this fashion. Electron micrographs of these replicas are shown elsewhere.[3] In no case that we encountered were parlodion-backed replicas stripped from surfaces that retained ethyl cellulose-backed films. Such surfaces included single monolayers of barium stearate applied to glass slides by the Blodgett-Langmuir technique;[4] ferric stearate films rubbed on glass;[4] and octadecylamine films deposited on glass from solution[5] in purified ligroin (b.p. 190–195 C).

In consideration of these results, we recommend that ethyl cellulose be used universally in shadow-cast replica techniques instead of parlodion. Since we do not have the opportunity to develop this technique further at present, we suggest that ethyl cellulose be tried particularly in those cases where parlodion-backed films are stripped only erratically, such as with platinum-palladium films or uranium films on glass.[1]

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** Contribution No. 1285.
[1] R. C. Williams and R. C. Backus, J. App. Phys. **20**, 98 (1949).
[2] A. Rothen, J. Biol. Chem. **168**, 75 (1947).
[3] S. J. Singer, to be published.
*** Obtained from Hercules Powder Company, Wilmington, Delaware, and designated N-22.
[4] K. B. Blodgett and I. Langmuir, Phys. Rev. **51**, 964 (1937).
[5] Bigelow, Pickett, and Zisman, J. Coll. Sci. **1**, 513 (1946).

The Subcooling of Liquid Metals

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VONNEGUT[1] has shown that an aggregate of very small droplets (1 to 10 microns) of liquid tin, separated by the oxide skin surrounding each particle, must be cooled 110 to 120°C below the thermodynamic liquid-solid transformation temperature before solidification proceeds rapidly.

We have made some observations on the rate of solidification of aggregates of mercury and gallium droplets. Collections of mercury droplets were prepared by dispersing mercury in solutions of sodium oleate in alcohol and in solutions of iodine in alcohol. In the latter, each mercury particle was coated with an iodide film. The particles averaged about 200 microns in diameter in the sodium oleate solution and about 50 microns in the iodine solution. The transformation was followed dilatometrically using alcohol as an indicator.

Starting about 20° above the melting point, T_m, samples were cooled about 10° an hour. After the transformation was completed the aggregate was slowly warmed through the melting temperature. Dilatometer readings were taken at close intervals in both the cooling and heating cycles. Mercury aggregates prepared by the first procedure did not show any measurable transformation until a temperature 33° below T_m had been reached. At this temperature the transformation was sluggish and probably confined to the larger particles. The rate of solidification became rapid at a temperature 39° below T_m. Aggregates held 22 degrees below did not transform after two hours.

Aggregates separated by the iodide film did not transform at a rapid rate until a temperature 46° below T_m had been attained. At 43° below T_m there was no appreciable transformation during a 1-hour holding period, except for 10 percent of the sample (probably the larger droplets) that transformed immediately.

Aggregates of gallium droplets were dispersed in alcoholic sodium oleate and the particles were about the same size as those of mercury in the same solution. The rate of solidification of gallium did not become appreciable until the gallium had been supercooled 70°C.

In Table I the maximum subcooling that has been obtained in bulk and in aggregates of small droplets are compared for tin, gallium, and mercury. It is interesting to note that the ratio T/T_m listed in the table, where T is the lowest absolute temperature to which the liquid has been subcooled, is roughly constant. Also shown in the table are liquid-solid interfacial energies σ calculated by the method of Fisher, Hollomon, and Turnbull.[2]

TABLE I.

Metal	Maximum subcooling °C: Bulk	Aggregates of small droplets	T/T_m	σ
Tin	31*	110**	0.78	65
Mercury	14*	46	0.80	23
Gallium	55	70	0.75	55

* Danilov and Neumark, Physik Zeits. Sowjet, union **12**, 313 (1937).
** See reference 1.

Calculations based on the theory of homogeneous nucleation[2] indicate that the increased subcooling attained by dispersing bulk samples into droplets cannot be accounted for by the decreased nucleation probability occasioned by decreasing the droplet size. Rather there is evidence that nucleation in bulk liquid samples is generally "catalyzed" at the surface of heterogeneties. In pure liquids these "nucleation catalysts" may be limited in number so that they are segregated on a small portion of the droplets when the sample is dispersed. These promote transformation only on the droplets in which they are localized. Transformation of particles containing no catalysts may occur by homogeneous nucleation which proceeds at measurable speeds at much lower temperatures.

[1] Vonnegut, J. Colloid Science **3**, 563 (1948).
[2] Fisher, Hollomon, and Turnbull, Science **109**, 168 (1949).

Measurement of the Dielectric Constant and Loss of Solids and Liquids by a Cavity Perturbation Method

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A CAVITY resonator method for the measurement of the dielectric constant and loss of small samples was given by Sproull and Linder.[1] This method is characterized by convenient measurement techniques, simple calculations, and direct extension to the measurement of the shunt impedance of a cavity. The present work was undertaken to extend the usefulness fo this method by increasing its accuracy with a sensitive technique for measuring small frequency differences.

1. Review of the theory.—Bethe and Schwinger have developde a perturbation theory[2] which gives the change in resonance frequency (f) and loaded $Q(Q)$ of a cavity due to some small change in the cavity. They consider two cavities, 1 and 2 which differ